IN THE U.S. PATENT AND TRADEMARK OFFICE

APPLICANT:	Kazuaki SUMITA et al.
SERIAL NO.:	10/808,329
FILED:	March 25, 2004
FOR:	Liquid Epoxy Resin Composition and Semiconductor Device
GROUP:	1712
EXAMINER:	SELLERS, ROBERT E

D E C L A R A T I O N

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir,

I, Kazuaki SUMITA, resident of c/o Silicone-Electronics Materials Research Center, Shin-Etsu Chemical Co., Ltd., 1-10, Hitomi, Matsuida-machi, Annaka-shi, Gunma-ken, Japan do hereby declare that:

1. I was graduated from Master Course of the Department of Material and Applied Chemistry of Nihon

University, Japan in March, 1992. Since 1992, I have been employed by Shin-Etsu Chemical Co., Ltd., the assignee of the above-identified application. I have been engaged in research and development relating to organic material (MC) in the laboratory of the Company

2. I am one of the named inventors of the above-identified application and hence, am familiar with the subject matter disclosed in said application.

3. In order to show the feature of the present invention, I conducted the following experiments.

[Experiments]

The components shown in Table 1 were mixed to uniformity on a three-roll mill to give various resin compositions. These resin compositions were examined by the following tests. The results are also shown in Table 1.

[Viscosity]

The viscosity at 25° C was measured using a BH-type rotary viscometer at a rotational speed of 4 rpm.

[Penetration test]

A polyimide-coated silicon chip of 10 mm × 10 mm was placed on a FR-4 substrate of 30 mm × 30 mm using spacers of approximately 50 μm thick, leaving a gap therebetween. The resin composition was melted on a hot plate at 100° C and allowed to penetrate into the gap. The time taken until the gap was fully filled with the composition was measured.

[Void test]

A polyimide-coated silicon chip of 10 mm × 10 mm was placed on a FR-4 substrate of 30 mm × 30 mm using spacers of approximately 50 μm thick, to form a flip chip package having a gap of approximately 50 μm. The composition was introduced into the gap and cured thereat. Using a scanning acoustic microscope C-SAM (SONIX Inc.), the sample was inspected for voiding.

[Toughness K_{1c}]

The toughness K_{1c} at normal temperature was measured according to ASTM D5045.

[Glass Transition Temperature (Tg)]

Using a sample of the cured composition measuring 5×5×15 mm, the glass transition temperature was measured with a thermomechanical analyzer at a heating rate of 5° C/min.

[Coefficients of Thermal Expansion (CTE)]

Based on the Tg measurement described above, a coefficient of thermal expansion below Tg (CTE-1) was determined for a temperature range of 50 to 80° C, and a coefficient of thermal expansion above Tg (CTE-2) was determined for a temperature range of 200 to 230° C.

[Bond strength test]

On a polyimide-coated silicon chip was rested a frustoconical sample having a top diameter of 2 mm, a bottom diameter of 5 mm and a height of 3 mm. It was cured at 150° C for 3 hours. At the end of curing, the sample was measured for (initial) shear bond strength. The cured sample was then placed in a pressure cooker test (PCT) environment of 121° C and 2.1 atm for 336 hours for moisture absorption. At the end of PCT test, shear bond strength was measured again. In each Example, five

samples were used, from which an average bond strength value was calculated.

[PCT peel test]

A polyimide-coated 10×10 mm silicon chip was stacked on a 30×30 mm FR-4 substrate using spacers of approximately 100 μm thick, to form a flip chip package having a gap of approximately 100 μm. An epoxy resin composition was introduced into the gap and cured thereat. The assembly was held at 30° C and RH 65% for 192 hours and then processed 5 times by IR reflow set at a maximum temperature of 265° C, before the assembly was checked for peeling. The assembly was then placed in a PCT environment of 121° C and 2.1 atm for 336 hours, before the assembly was checked for peeling. Peeling was inspected by C-SAM (SONIX Inc.).

[Thermal shock test]

A polyimide-coated 10×10 mm silicon chip was stacked on a 30×30 mm FR-4 substrate using spacers of approximately 100 μm thick, to form a flip chip package having a gap of approximately 100 μm. An epoxy resin composition was introduced into the gap and cured thereat.

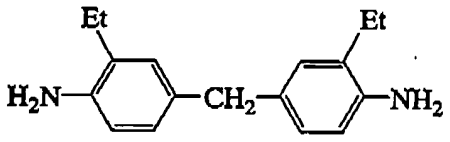
The assembly was held at 30° C and RH 65% for 192 hours and then processed 5 times by IR reflow set at a maximum temperature of 265° C. The assembly was then tested by thermal cycling between -65° C/30 minutes and 150° C/30 minutes. After 250, 500 and 750 cycles, the assembly was examined for peeling and cracks.

Components

C-100S: diethyldiaminophenylmethane,
Nippon Kayaku Co., Ltd.

C-300S: tetraethyldiaminophenylmethane,
Nippon Kayaku Co., Ltd.

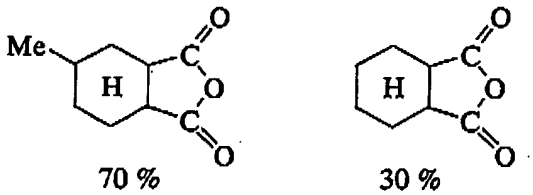
Seikacure-S: 4,4'-diamine-dibenzen-sulfone,
Wakayama Seika Kogyo Co., Ltd.

KAYAHARD AA: 

,
Nippon Kayaku Co., Ltd.

RE303S-L: bisphenol F-type epoxy resin,
Nippon Kayaku Co., Ltd.

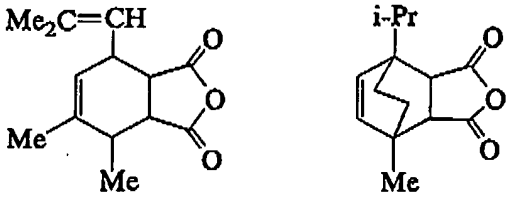
MH700:



70 % 30 %

New Japan Chemical Co., Ltd.

YH307:



40 % 60 %

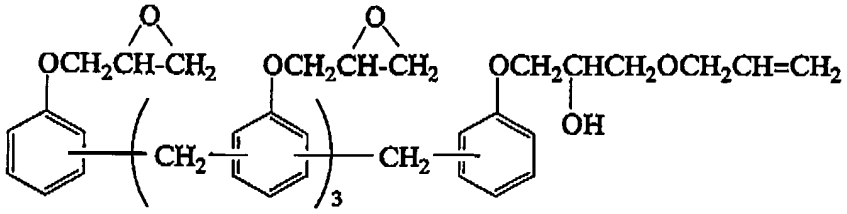
(Me is methyl group and i-Pr is iso-propyl group)

Japan Epoxy Resins Co., Ltd.

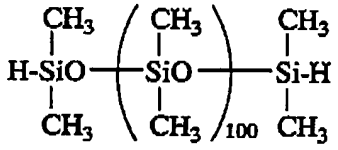
KBM403: silane coupling agent, γ-glycidoxypropyltrimethoxysilane, Shin-Etsu Chemical Co., Ltd.

Spherical silica: spherical silica having a maximum particle size of up to 24 μm and an average particle size of 6 μm

Copolymer: the addition reaction product of



and



2E4MZ: 2-ethyl-4-methylimidazole,
Shikoku Chemicals Corporation

Solvent A: 2-ethoxyethyl acetate,
boiling point 156.3° C

Solvent B: 2-butoxyethyl acetate, boiling point 192° C

Table 1-1

Component (pbw)		Invention								
		1	2	3	4	5	6	7	8	9
C-100S		30			15					
C-300S			35		20	25				
Seikacure-S				32		10				
KAYAHARD AA							35	32	35	32
RE303S-L		70	65	68	65	65	65	68	65	68
MH700										
YH307										
Spherical silica		150	150	150	150	150	150	150	150	150
KBM403										
Copolymer		4	4	4	4	4	4	4	0	0
2E4MZ										
Solvent A		3	3	3	3	3	3	3		
Solvent B									3	3
Measurement results										
Molar ratio of liquid epoxy resin (A) to aromatic amine curing agent (B): (A)/(B)		0.84	0.84	0.78	0.78	0.80	0.70	0.80	0.70	0.80
Viscosity (Pa·s @25°C)		75.6	56.6	66.3	72.5	73.4	22.0	20.5	14.6	13.1
Void test		nil	nil	nil	nil	nil	nil	nil	nil	nil
Toughness K_{1c}		4.3	4.2	4.1	4.3	4.2	3.9	4.2	3.8	4.0
Tg (°C)		125	122	110	105	108	102	102	102	103
CTE-1 (ppm/°C)		32	31	33	32	31	32	32	32	31
CTE-2 (ppm/°C)		122	115	113	114	119	116	114	115	116
PCT peel test	After 5 times of IR reflow at 265°C	no peeling	no peeling	no peeling	no peeling	no peeling	no peeling	no peeling	no peeling	no peeling
	After PCT 336 hr	no peeling	no peeling	no peeling	no peeling	no peeling	no peeling	no peeling	no peeling	no peeling
Bond strength (kgf/cm^2)	Initial	256	248	255	243	255	229	231	215	221
	After PCT 336 hr	206	199	203	187	189	175	172	184	179
Failure (%) after thermal shock test	250 cycles	0	0	0	0	0	0	0	0	0
	500 cycles	0	0	0	0	0	0	0	0	0
	750 cycles	0	0	0	0	0	0	0	0	0

Table 1-2

Component (pbw)		Comparison					
		1	2	3	4	5	6
C-100S			20	40	27		28.2
C-300S							
Seikacure-S							
KAYAHARD AA			-	-	-	27	
RE303S-L		50	80	60	72	73	71.8
MH700		30				-	
YH307		20					
Spherical silica		150	150	150	150	150	150
KBM403		1.0					
Copolymer		4	4	4	4	4	4
2E4MZ		1					-
Solvent A			3	3	3	3	3
Solvent B							
Measurement results							
Molar ratio of liquid epoxy resin (A) to aromatic amine curing agent (B): (A)/(B)		-	1.12	0.55	1.00	1.00	0.95
Viscosity (Pa·s @25°C)		28.4	64.3	108	66.8	12.4	66.8
Void test		nil	nil	nil	nil	nil	nil
Toughness K_{1c}		2.6	3.4	2.9	3.3	3.4	3.3
Tg (°C)		140	138	86	139	110	133
CTE-1 (ppm/°C)		31	29	35	29	32	30
CTE-2 (ppm/°C)		113	105	144	110	115	108
PCT peel test	After 5 times of IR reflow at 265°C	peeled	no peeling	peeled	no peeling	no peeling	no peeling
	After PCT 336 hr	peeled	peeled	peeled	no peeling	no peeling	peeled
Bond strength (kgf/cm^2)	Initial	182	198	133	205	215	159
	After PCT 336 hr	95	95	56	121	154	73
Failure (%) after thermal shock test	250 cycles	50	0	0	0	0	0
	500 cycles	100	0	40	0	0	0
	750 cycles	-	10	100	5	5	5

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Dated this 2nd day of Aug. , 2006